Synopsis

Development & Applications of 3D Printing Resins From Renewable Resources

By

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In

CHEMISTRY

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1. Introduction

The 3D printing is emerging technology for manufacturing of complex, user specified, cost effective and high precision components using computer aided designs (CAD) [1]. It offers low material waste and less energy for production. The materials are used in printing can be metals, polymers, ceramics, food and even living cells. The method of building of 3D objects is an addition of materials layer by layer in 2d slices, also called as additive manufacturing (AM). Different techniques developed in order to print using various materials, which are fused deposit modeling (FDM), selective laser sintering (SLS), Stereolithography (STL), inkjet printing, and Laminated Object Manufacturing (LOM) [2]. The advantages of AM over traditional manufacturing technology are that its ability to produce complex shapes and designs of products. In addition, products are prepared in low cost and less time. 3D printing finds applications mainly in areas biomedical, aerospace, automotive, engineering and arts. The lightweight parts are now possible to manufacture in automotive and aerospace industry, while securing safety issues using AM technologies[3]. Additive manufacturing technologies can supply architects powerful tool for creating a physical model faster without worrying about the complexity of their design. It also achieves a better resolution than other processes used in architecture. Architects work with CAD software, so there is no need for them to adapt to anything because the STL file is created from a CAD file. Stereolithography is a method suitable for the architectural modeling because of accuracy and printing resolution[4]. In most AM methods resolution of material in between 50-200µm, where as Stereolithography method less than 20µm and far better accuracy than other 3D printing techniques. Stereolithography setups using two-photon initiations process < 300nm resolution is achieved [5].In Stereolithography process the liquid resin is used for making objects, The photocurable property of a resin makes it solidified or cured when contact

with UV radiation. The process starts with the model in CAD software later it is converted into STL file, in which object is cut in slices containing information about the each slice which is printed layer by layer. Production of current Stereolithography Resins from petroleum compounds, it has limited sources and has the adverse effect on the environment. Bio-based polymers are materials which are produced from renewable resources. The worldwide interest in bio-based polymers has accelerated in recent years due to the desire and need to find non-fossil fuel-based polymers. In addition, they have positive environmental impacts such as reduced carbon dioxide emissions. Biopolymers are biodegradable in the limited time using soil bacteria and fungi which will control waste garbage problem and related environmental issues. It is expected that biopolymers will reach world market share for just over 10% of polymers by 2020 from 3% in 2015 (Frost and Sullivan). The exploitation of renewable resources in the production of polymers is delivered increasing attention due to concerns about the environmental sustainability. Nowadays, most commercially available polymers are derived from non-renewable resources and account worldwide for approximately 7% of all oil and gas used. With the continuous depletion of fossil oils, dramatic fluctuations in the oil prices and environmental concerns, there is a burning need to develop eco-friendly polymeric materials from biobased resources. Biopolymers produced from biomass offers unique properties in combination with 3D printing. The advantages of objects producing from biomaterials are a) Local production of biomaterials and products, b) Zero greenhouse gas emissions, c) Unique innovative new and sustainable product, and d) The realization of a sustainable and circular economy. This research will focus on emphasizes production of renewable based resins, biopolymers which are suitable in the 3D printing process. The Project aims to establish manufacturing technology for preparation of 3D printing resin from renewable resources. The Renewable resources as plant oil,

cellulose, starch, lignin etc will be used as starting material. 3D printing resin having curing properties (thermal or photocurable) will be prepare. The developed biopolymer/resin will be tested in the 3D printer to prepare objects. The process will be affordable and cost effective and economical. The main advantage of process will be local resources will be used for development of 3D printing resin so that local economy will get boosting

3D printing with Biomaterials

- Local production of both biomaterials and products
- Zero greenhouse gas emissions
- Unique, Innovative, new and sustainable products
- The realization of a sustainable and circular economy
- Material from biological origin instead of fossil fuel
- No CO2 (short cycle) emissions
- Feedstock can grow everywhere
- Every plastic can be produced
- Specific and unique characteristics for 3D printing

2. Literature review

Stereolithography was the first 3D printing technology developed in 1980 by Charles Hull. The other AM methods were established over the 20 years. In Stereolithography Printer the photo-

curable liquid resin is spatially printed into three-dimensional solid object controlled by light beams which are in UV range using computer aided designs (CAD) [4]. The relatively lower number of commercial Stereolithography Resins is the main limitation of this technology. Acrylate, epoxy, and polyurethane based Stereolithography Resins are the commonly available, where as the Acrylate-based resins are the wide applications range and higher properties compare to Epoxy and polyurethane based resins [5]. Most of the Stereolithography Resins are petroleum based, nondegradable which are harmful to the environment, as well as expensive and biocompatibility is also the issue of these resins [6]. Ever increasing demand for bio-based and renewable products is the cause to develop our interest in Stereolithography resin on bio-based monomers and polymers [7]. In early literature, the soybean oil was converted into soybean acrylate and solidified using 3D printing technique into smart and highly biocompatible scaffold for tissue engineering [8].The novel Chitosan-based biocompatible resin with polyethylene glycol diacrylate was formulated using Stereolithography ear-shaped scaffolds was prepared [9].

3. Objective of research work

The research work focused mainly on following objectives, on which PhD work will carry out

1) To identify the suitable renewable resource useful for development of 3D printing resin.

2) To develop the biopolymer/resin from renewable resources

3) To synthesize and characterize the biopolymer/resin

4) Test the biopolymer/resin in 3D printing apparatus using (thermal/UV-curable method

5) The Renewable resources as plant oil, cellulose, starch, lignin etc will be used as starting material.

6) The main advantage of process will be local resources will be used for development of 3D printing resin so that local economy will get boosting.

3.1. Expected Outcomes

1) The project will provide suitable method for synthesis & characterization of biopolymer/resin having properties suitable for 3D printing.
2) The Technology development with scientific foundation in all steps of the renewable resource to 3D printed object.
3) Affordable products useful for industrial and domestic use will be prepared using local resources.

This project will collaboratively produce new scientific knowledge in the form of joint publications, joint-owned patents, and other public goods, which will advance the 3D printing technology available in the country and contribute to the rural economy.

4. Methodology:

The methods are adopted for synthesis and characterization of the STEROLITHOGRAPHY resins are following:

4.1. Acrylation reaction on renewable resources:

The acrylation reaction can be done on the functional groups or incorporated functional groups present on the molecules which is based on renewable resources (plant oils, lignin, cellulose, Chitosan...) the acrylated compounds or molecules will be used for generation Sterolithography resins.

4.2. Epoxidation reaction:

The epoxidation is done on plant oil and double bonds containing compounds from renewable resources, using Hydrogen peroxide or other epoxidation catalyst.

4.3. Thiol-ene reaction:

Multifunctional thiolated compound added on biobased compounds by free radical mechanisms, the coupling is taken place UV radiation or thermal methods.

5. Importance of study

5.1. International Status

The worldwide 3D printing industry is now expected to grow from $3.07 billion in revenue in 2013 to $12.8 billion by 2018, and exceed $21 billion in worldwide revenue by 2020. Wohlers Report 2013 had forecast the industry would grow to become a $10.8 billion industry by 2021.

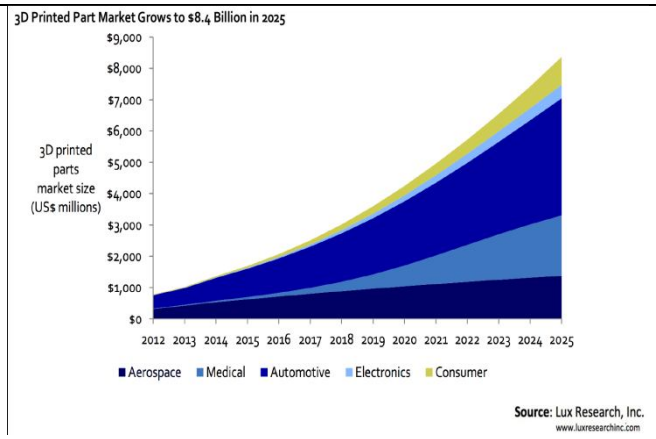

Fig 1: Global 3D printing industry forecast

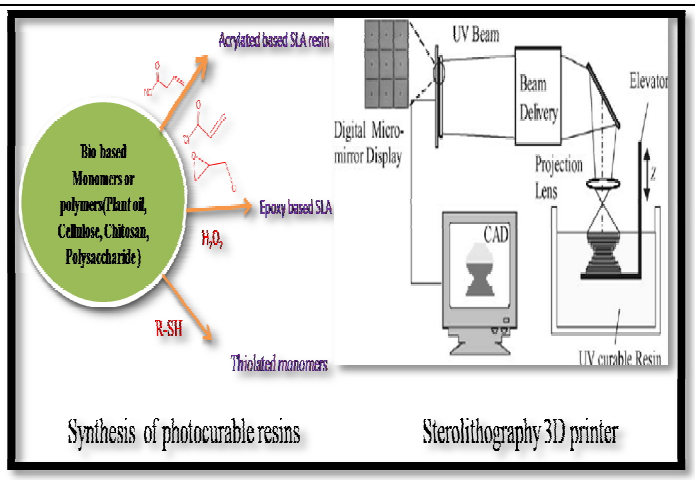

Fig 2: Methodolgy adopted for synthesis SLA resins

5.2. National status

Low cost 3D printing resins from renewable source as alternative source.

5.3 Significance of the study

Our project study is based on a view to prepare Sterolithography resin from the renewable resource materials. The polymers derived from renewable resource materials are steadily and rapidly gaining their rightful status among macromolecular materials. They have suitable compositions, which can be utilized for the development of various chemicals and polymers. Furthermore, they are sustainable, biodegradable and offer several possibilities of applications that can rarely be met by the petroleum based resources. biobased polymers are biodegradable and environment friendly. Plants consume carbon dioxide and help in reducing the green house gases. Among the various plant seed oils, non-edible oils have been used for the development of chemicals and polymers thus avoids food *vs.* fuel predicament.

The present technology highlights the development of Sterolithographic resin from the Bio-based sources namely plant oils, cellulose, lignin, chitosan etc. These renewable sources were obtained from abundantly available renewable plant resources and were used as carbon source to develop different types of oleo chemicals, monomers, polymers, composites and blends. The products traditionally obtained from petroleum based products have been replaced consists of flexible elastomeric films, fibre-composite, coatings, printing ink, encapsulant, adhesives, sealants, mounting agents, and casting resin. The polymers prepared from various sources of plant oil are biodegradable under compost conditions, biocompatible, non-toxic (tested on cell lines) and can be transformed to soil as fertilizers. The other advantage material is that they are biocompatiable and can be very useful for health care industry for making personalized implants and drug dosing.

6. Proposed work Plan

Activity (months)	0	3	6	12	18	24	30	36
Litreture study, course work								
Pilot scale batch for monomers from starting material								
Testing of product & Distribution of final product in market								
Feedback/suggestions on product from customers & improvement of process as per customer suggestions								
Repeating pilot higher scale batch for resin formation								
Development of other applications (coatings, composite and casting) for commercial application Repeating pilot higher scale batch for resin formation								
Economics of feasibility study for commercialization								
Comprehensive study report of the project findings								

7. References

1) Bajaj, P., R. M. Schweller, A. Khademhosseini, J. L. West, and R. Bashir. 3D biofabrication strategies for tissue engineering and regenerative medicine. Annu. Rev. Biomed. Eng. 16:247–276, 2014.

2) Kumar,S., & Kruth, J.-P., Composites by rapid prototyping technology, Materials and Design 31: 850–856, 2010.

3) K. U. Bletzinger and E. Ramm, “Structural optimization and form finding of light weight structures,” Computers and Structures, vol. 79, no. 22–25, pp. 2053–2062, 2001.

3) Melchels, F.P.W., Feijen,J., & Grijpma,W.D. A review on stereolithography and its applications in biomedical engineering. Biomaterials 31:6121-6130,2010.

4) C. Semetay, Laser engineered net shaping (LENS) modeling using welding simulation concepts [ProQuest Dissertations and Theses], Lehigh University, 2007.

5) Castro, N. J., O'Brien, J., & Zhang, L. G., Integrating biologically inspired nanomaterials and table-top stereolithography for 3D printed biomimetic osteochondral scaffolds. Nanoscale, 7: 14010-14022, 2015.

6) Esposito Corcione, C., Greco, A. & Maffezzoli, A.,Photopolymerization kinetics of an epoxy-based resin for stereolithography. Journal of Applied Polymer Science, 92, 3484-3491,2004.

7) Huang, S.H., Liu,P.,Mokasdar, A., Hou ,L. Additive manufacturing and its societal impact: a literature review.

8) Miao, S., Wang, P., Su, Z. & Zhang, S. Vegetable-oil-based polymers as future polymeric biomaterials. Acta Biomater. 10, 1692–1704, (2014).

9) Shida Miao, W. Z., Castro,N. J., Nowicki, M., Zhou X., Cui .H., Fisher J. P., and . Zhang, L. G, 4D printing smart biomedical scaffolds with novel soybean oil epoxidized acrylate. Scientific reports, 2016. 6.

10) Morris,V.B., Nimbalkar, S.,Mousa, Y., Mcclellan,P., and Akkus,O., Mechanical Properties, Cytocompatibility and Manufacturability of Chitosan:PEGDA Hybrid-Gel Scaffolds by Stereolithography, Annals of Biomedical Engineering,2016. http://dx.doi.org/10.1007/s10439-016-1643-1.